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Published in:
Macromolecules

DOI:
10.1021/ma0115850

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2002

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Boiteau, L., Moroni, M., Hilberer, A., Werts, M. P. L., de Boer, B., & Hadziioannou, G. (2002). Synthesis of a diblock copolymer with pendent luminescent and charge transport units through nitroxide-mediated free radical polymerization. *Macromolecules*, *35*(5), 1543 - 1548. https://doi.org/10.1021/ma0115850

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Synthesis of a Diblock Copolymer with Pendent Luminescent and Charge Transport Units through Nitroxide-Mediated Free Radical Polymerization

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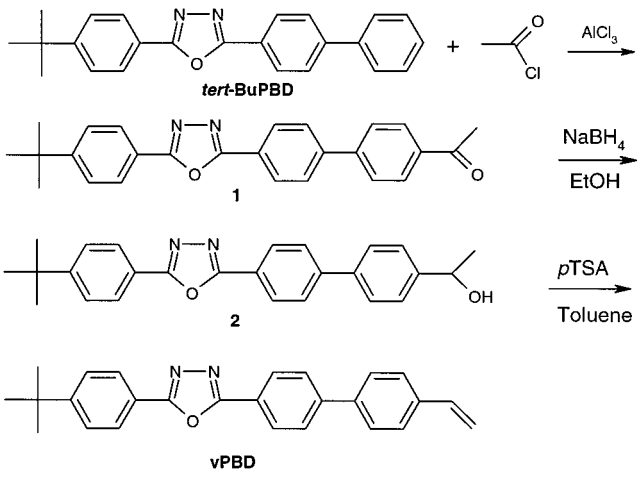
Received September 7, 2001; Revised Manuscript Received November 26, 2001

ABSTRACT: We present the efficient polymerization of a vinyl monomer bearing electron-transporting units, 2-[4-(4′-vinylbiphenylyl)]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (vPBD), by using a TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)-mediated radical polymerization method. A kinetic study using this monomer showed a quasi-living free radical character. The corresponding homopolymer was obtained in high yield with a very narrow polydispersity. Further reaction of the isolated polymer with another vinyl monomer bearing luminescent groups, 4-*tert*-butyl-4′-(4-vinylstyryl)-*trans*-stilbene (v3PV), gave a diblock copolymer containing both functional groups.

Introduction

Among the various techniques to polymerize vinyl monomers, ranging from ionic to group transfer, the most convenient remains free radical polymerization. Its mild reaction conditions and the wide range of polymerizable monomers make it suitable for both industry and research laboratories. However, the main disadvantage of classical free radical polymerization is that it does not allow architecture and structure control. The obtained polymers are generally polydisperse, the molecular weights are difficult to control, and there is no possibility to make block copolymers. These features are indeed accessible through living anionic or cationic processes, but these techniques require rigorous conditions and delicate procedures. In the past decade there have been many efforts toward the development of "living" free radical polymerization processes. Three successful and commonly used approaches were introduced, namely iniferters[1−3] (*ini*tiator−chain trans*fer*−*ter*minator), atom transfer radical polymerization (ATRP),[4] and nitroxide-mediated free radical polymerization (NMRP).[5−8] These techniques employ the principle of an equilibrium between a low concentration of active radicals and a rather large number of dormant species. This suppresses bimolecular side reactions such as recombination or disproportionation to such a degree that the overall polymerization process shows "living" characteristics, e.g., the increase of the molecular weight with conversion, and the possibility to synthesize block copolymers and other complex macromolecular architectures.[8−10] NMRP utilizes stable free radicals, such as nitroxides, as reversible terminating agents to control the polymerization. The superiority of this method, when compared to other living processes, comes from the stability of the end-capping groups, which enables isolation of a polymer with "dormant" chain ends that can later be reactivated. The use of this technique for the synthesis of copolymers of styrene and acrylonitrile[11] or *N*-cyclohexylmaleimide[12] was recently reported. With the development of novel nitroxides,[13] a wide variety of monomers, e.g., acrylates, acrylonitrile, 1,4-butadiene, and derivatives thereof, became available to the chemist for the use in NMRP. However, only very few monomers have so far been shown to be reactive toward nitroxide-mediated free radical polymerization based on 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). In our previous work we demonstrated the functionalization of a poly(*p*-phenylenevinylene) (PPV) block with a TEMPO initiator and its use in the synthesis of rod−coil block copolymers. The controlled radical polymerization of the coil (polystyrene) block leaves the PPV moiety untouched.[14] Furthermore, we incorporated an electron-accepting moiety (C_{60}) in the coil block, resulting in a donor−acceptor block copolymer.[14a,15]

Scheme 1. Synthesis of Monomer 2-[4-(4′-Vinylbiphenylyl)]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (vPBD)



We have also demonstrated that the NMRP technique can be used in dilute solution to polymerize a large functional monomer.[16] From the conjugated monomer 4-*tert*-butyl-4′-(4-vinylstyryl)-*trans*-stilbene (v3PV, Scheme 2), we obtained a well-defined polymer, with narrow polydispersity, having blue-light-emitting side chains. This oligo(phenylenevinylene) side chain can be

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10.1021/ma0115850 CCC: $22.00 © 2002 American Chemical Society
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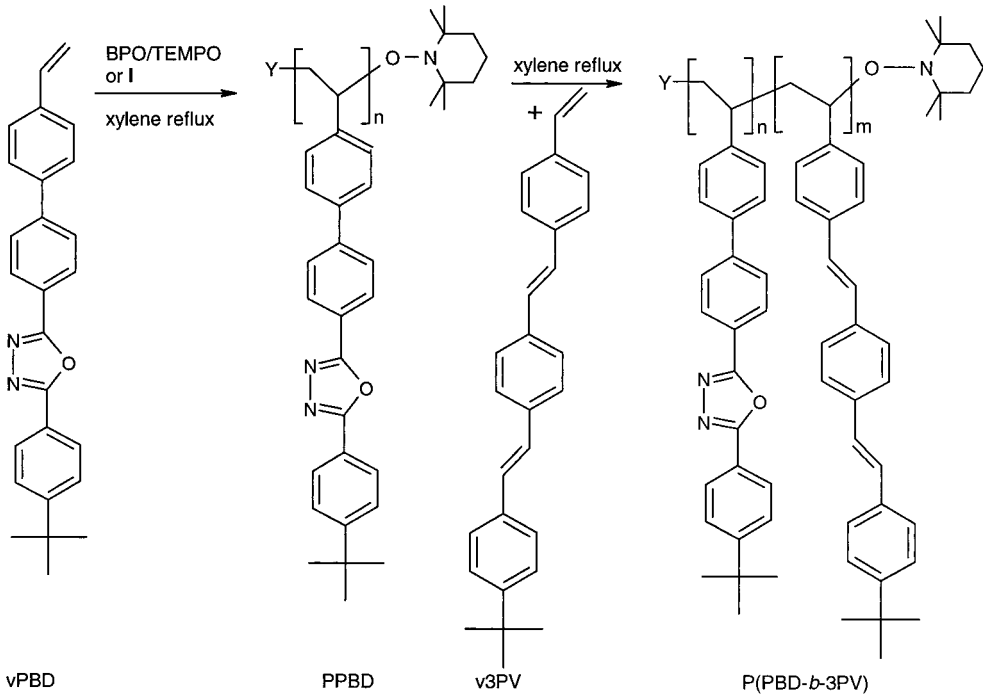
Scheme 2. Synthesis of PPBD Homopolymer and Subsequent Extension to P(PBD-*b*-3PV) Diblock Copolymer. Y = PhCOO− for BPO/TEMPO and Y = H for (I)



readily fine-tuned over a wide range by the addition of functional groups[17] or by increasing its length. Cacialli et al. used a similar approach to incorporate side chains of distyrylbenzene and 2-(4-biphenylyl)-5-phenyl-1,3,4-oxadiazole (PBD), a molecule well-known for its electron transport properties, into poly(methacrylate) copolymer analogues.[18] Similarly, Jiang et al. synthesized statistical copolymers with side-chain hole- and electron-transporting groups that demonstrated good efficiencies in dye-doped devices.[19]

The incorporation of oxadiazole-based side chains into PPVs was found to improve the electroluminescent properties of PPVs, due to the improved electron-transporting properties of the conjugated polymer.[20−23] Peng et al. introduced oxadiazole repeat units in the backbone of a conjugated polymer, creating polymers of alternating phenylenevinylene and oxadiazole moieties.[24,25]

In this paper we extend the work on PBD-based monomers. The molecule was functionalized with a terminal vinyl group to give 2-[4-(4′-vinylbiphenylyl)]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (vPBD, Scheme 1), and its polymerization was studied with a 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)/dibenzoyl peroxide (BPO) mixture or a TEMPO−ethylbenzene derivative (**I**) as initiator (Scheme 2). Further reaction of the isolated homopolymer (PPBD) with the v3PV monomer[16] enabled the preparation of a diblock copolymer, P(PBD-*b*-3PV), as shown in Scheme 2.

Experimental Section

Materials. Aluminum chloride, acetyl chloride, 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (*tert*-BuPBD), sodium borohydride, *p*-toluenesulfonic acid monohydrate (*p*TSA), (1-bromoethyl)benzene, 10-camphorsulfonic acid (CSA), silica gel, deuterated chloroform, and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) were obtained from Aldrich. Dibenzoyl peroxide (BPO), sodium, hydrochloric acid, ethanol, methanol, tetrahydrofuran, methylene chloride, toluene, and xylene were obtained from Merck. BPO was recrystallized from chloroform/methanol before use.

The monomer vPBD was prepared in three steps starting with the commercially available PBD, by adapting a method previously reported in the literature (Scheme 1).[26] The unimolecular initiator (**I**) used in later experiments was synthesized according to literature method by reacting sodium−TEMPO salt on (1-bromoethyl)benzene.[10] The synthesis of v3PV monomer was described previously.[16]

2-[4-(4′-Vinylbiphenylyl)]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (vPBD). 2-[4-(4′-Acetylbiphenylyl)-5-(4-*tert*-butylphenyl)]-1,3,4-oxadiazole (**1**): The *tert*-BuPBD (15 g, 42 mmol) was dissolved under argon in 380 mL of dry methylene chloride. Freshly distilled acetyl chloride (7.6 mL, 107 mmol) was added while stirring. Aluminum chloride (48 g, 360 mmol) was then slowly added, and the mixture was heated to reflux for 5 h. The cooled mixture was poured on 300 g of ice. The organic phase was washed twice with 200 mL of water and dried over Na_2SO_4. The solvent was evaporated to obtain 16 g (40.35 mmol) of crude product, which could be used without further purification. ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.21 (d, 2H, Φ*H*), 8.06 (2d, 4H, Φ*H*), 7.79 (2t, 4H, Φ*H*), 7.58 (d, 2H, Φ*H*), 2.64 (s, 3H, −COCH_3), 1.37 (s, 3H, −Φ−CH_3).

2-[4-(4′-(1-Hydroxyethyl)biphenylyl)]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (2). To a stirred solution of the ketone **1** (3.01 g, 7.6 mmol) in 70 mL of ethanol was slowly added $NaBH_4$ (0.68 g, 18 mmol). The mixture was stirred for 5 h at room temperature. 20 mL of 2% HCl solution was added, and the precipitate was filtered off and washed with water to give 2.99 g (7.5 mmol) of product **2** that could be used without further purification. ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.19 (d, 2H, Φ*H*), 8.07 (d, 2H, Φ*H*), 7.77 (d, 2H, Φ*H*), 7.61 (d, 2H, Φ*H*), 7.54 (dd, 4H, Φ*H*), 4.96 (qu, 1H, −C*H*OH−), 1.70 (s, 1H, −O*H*), 1.58 (d, 3H, −CHOH−CH_3), 1.36 (s, 9H, Φ−CH_3).

2-[4-(4′-Vinylbiphenylyl)]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (vPBD). A solution of **2** (2.31 g, 5.80 mmol) and *p*TSA (115 mg; 0.61 mmol) in 80 mL of dry toluene was heated to reflux in a Dean−Stark apparatus. The distilled solvent was continuously removed, while same amounts of dry toluene were added to the reaction. The reaction was followed by TLC and continued until complete conversion (ca. 18−24 h). The solution was then allowed to concentrate to ca. half the volume, and the cooled mixture was mixed with 30 mL of chloroform and washed twice with 30 mL of 1 N aqueous Na_2CO_3 and twice with 40 mL of water. The organic layer was dried over Na_2SO_4, evaporated, and then purified by column chromatog-

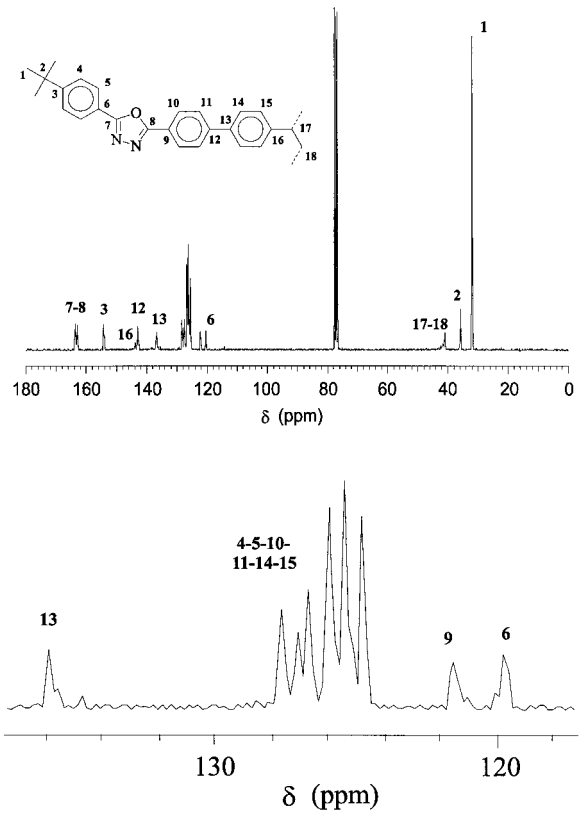


Figure 1. ^{13}C NMR spectrum of polymer PPBDa in $CDCl_3$.

raphy (silica gel, $CHCl_3$) to obtain 1.70 g (4.47 mmol) of monomer vPBD as a white powder. Overall yield: 70%. ^1H NMR ($CDCl_3$): δ (ppm) = 8.2 (d, 2H, Φ*H*), 8.09 (d, 2H, Φ*H*), 7.76 (d, 2H, Φ*H*), 7.58 (m, 6H, Φ*H*), 6.76 (qu, 1H, Φ−C*H*═CH_2), 5.82 (d, 1H, −CH═C*H*$_2$), 5.33 (d, 2H, −CH═C*H*$_2$), 1.37 (s, 9H, Φ−C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 164 (2 peaks, C7−C8), 155 (C3), 144 (C12), 139 (C16), 137 (C13), 136 (C17), 128−125 (6 peaks, C4−C5−C10−C11−C14−C15), 121 (C6), 123 (C9), 114, (C18), 36 (C2), 32 (C1).

Anal. Calcd. %: C, 82.07; H, 6.36; N, 7.36; O, 4.20; Found: C, 81.61; H, 6.44; N, 7.19; O, 4.52. The carbon atom numbering in the monomer exactly refers to that of the monomer unit in the polymer structure (Figure 1).

Synthesis of the Unimolecular Initiator (1-TEMPO-ethyl)benzene (I). Prepared according to Catala et al.[28] To a solution of 600 mg (3.8 mmol) of TEMPO in 40 mL of dry THF was added 180 mg (7.8 mmol) of finely cut sodium. The suspension was submitted to ultrasound while cooling with a water bath, until it completely decolorized (ca. 1 h). After 5 min standing, the clear solution was transferred to a solution of (1-bromoethyl)benzene (3.66 mmol, 0.5 mL) in 30 mL of dry THF. The suspension was stirred overnight at room temperature and then filtered. After solvent evaporation, the crude product was purified by chromatography (eluent hexane/dichloromethane 4/1) to afford 560 mg (2.15 mmol, 58%) of **I**, whose spectral data were identical to those found in the literature.[28]

Polymerizations. The polymers described were synthesized through a TEMPO-mediated "living" free radical process (Scheme 2). This method, which was initially described for simple monomers like styrene, is usually conducted in the bulk. However, the high melting points of our monomers make it necessary to run the polymerization in solution. Hot xylene is a good solvent for the monomers, its boiling point (140 °C) being well adapted to TEMPO-mediated polymerization. This route was previously used with v3PV, which showed no significant thermal polymerization under these reaction conditions.[16] We first prepared the PPBD homopolymers by refluxing the monomer and the initiator, either a BPO/TEMPO mixture (PPBDa−b) or the unimolecular initiator (**I**) (PPBDc−d), in xylene. Kinetic studies were performed using both initiating systems (PPBDb,d). A blank polymerization experiment (PPBDe) without initiator was also performed. To prepare the diblock P(PBD-*b*-3PV), the isolated PPBDa polymer and the v3PV monomer were refluxed together in xylene (Scheme 2).

PPBDa. The monomer vPBD (1.52 g, 4 mmol), BPO (2.4 mg, 0.01 mmol), the TEMPO radical (3.8 mg, 0.024 mmol), CSA (20 mg, 0.086 mmol), and 5 mL of xylene were charged under argon in a vessel, stirred at 95 °C for 1 h, and then refluxed for 16 h. The product was directly precipitated in 50 mL of methanol. The precipitate was collected, dissolved in 5 mL of warm toluene, and reprecipitated in 50 mL of methanol. The precipitate was collected by filtration and dried under vacuum to obtain 0.89 g of a white powder PPBDa. Yield: 59%. ^{13}C NMR ($CDCl_3$): δ (ppm) = 163−164 (2 peaks, C7−C8), 155 (C3), 144−143 (C12−C16), 137 (C13), 128−125 (6 peaks, C4−C5−C10−C11−C14−C15), 121 (C6), 123 (C9), 41 (C17−C18), 36 (C2), 32 (C1).

Anal. Calcd. %: C, 82.07; H, 6.36; N, 7.36; Found: C, 81.42; H, 6.50; N, 7.11.

PPBDb. The same procedure as above was followed with half the quantities of reagents (monomer, initiator) in 3 mL of xylene. After 1, 2.5, and 16 h, 0.5 mL aliquots were taken and precipitated in 10 mL of methanol. After 48 h, the remaining solution was precipitated in 20 mL of methanol. All the precipitates were dissolved in methylene chloride and reprecipitated in methanol.

PPBDc. Same procedure as above, with initiator **I** (9.9 mg, 0.038 mmol) and vPBD (1.4 g, 3.68 mmol) in 5 mL of xylene, refluxing for 15 h. The hot reaction mixture was precipitated in 20 mL of methanol. The precipitate was collected, dissolved in 5 mL of hot toluene, and reprecipitated in 20 mL of methanol to afford 850 mg of polymer.

PPBDd. Same procedure as for PPBDc, with **I** (4.7 mg, 0.018 mmol) and vPBD (940 mg, 2.47 mmol) in 4 mL of xylene, refluxing for 48 h. At different times, 0.5 mL aliquots were taken, precipitated once in 10 mL of methanol, filtered, and dried in a vacuum. The precipitates were dried and weighed, and the polymer/monomer ratio was determined by ^1H NMR.

PPBDe (Self-Initiated). vPBD (50 mg, 0.13 mmol) only in 0.2 mL of xylene, refluxing for 15 h. The mixture was diluted to 1 mL in toluene and precipitated in 5 mL of methanol. The precipitate was collected, dissolved in 5 mL of hot toluene, and reprecipitated in 20 mL of methanol.

Diblock Copolymer P(PBD-*b*-3PV). The polymer PPBDa (300 mg, 0.79 mmol of repeating units), the v3PV monomer (350 mg, 0.96 mmol), CSA (10 mg, 0.043 mmol), and 5 mL of xylene were charged under argon in a vessel. The mixture was stirred and refluxed for 3 days. The product was then precipitated in 30 mL of methanol, and the precipitate was collected by filtration to obtain 480 mg of a light yellow-beige powder. Anal. Calcd for a polymer containing $^2/_3$ of PBD and $^1/_3$ of 3PV (according to SEC values), %: C, 85.38; H, 6.81; N, 4.98; Found: C, 84.53; H, 7.04: N, 4.72.

Measurements. All the polymers are white or pale beige solids. PPBD polymers are well soluble in solvents such as THF, CH_2Cl_2, $CHCl_3$, toluene, and xylene. The P(PBD-*b*-3PV) diblock exhibits poorer solubility. Hot toluene and xylene may be considered to be the best solvents.

NMR Spectroscopy. ^1H and ^{13}C NMR spectra were collected at room temperature on a Varian (VXR 300) spectrometer with chloroform-*d* as solvent and internal standard. The spectra of the polymers show typical broad resonances. The ^1H NMR spectra show no peaks in the region of the vinyl hydrogen resonances. The ^{13}C NMR spectrum of PPBDa is given in Figure 1. The peaks of the vinyl carbons of the monomer at 136 and 114 ppm are not present anymore. The peak of the carbon C16, in α position of the polymer chain (formerly in α position of the double bond in the monomer), is shifted from 139 to 144 ppm, and a broad resonance appears at about 41 ppm, related to the carbon atoms of the polymer main chain. The six peaks corresponding to the signals of the sp^2 carbon atoms of the three phenyl rings (twice six different carbons) of the PBD group appear clearly on the PPBDa

Table 1. Results on VPBD Polymerization in Refluxing Xylene, Using TEMPO/BPO (PPBDa−b) or I (PPBDc−d) as Initiator[a]

run	initiator	reaction time (h)	conv (%)	M_w (g/mol)	poly-disp	theor M_w
PPBDa	BPO/TEMPO	16	59	38 000	1.21	45 000
PPBDb	BPO/TEMPO	1		43 000	1.34	
		2.5		54 000	1.46	
		16		63 000	1.29	
		48		65 000	1.31	
PPBDc	**I**	15	61	26 000	1.3	23 000
PPBDd	**I**	0.8	18	16 000	1.13	9 400
		2	23	20 000	1.12	12 000
		4	42	24 000	1.14	22 000
		17	56	31 500	1.29	29 000
		50	60	32 000	1.25	31 000
PPBDe		15	80	120 000	2.6	

[a] Molecular weight, polydispersity, and conversion (PPBDb: not measured) vs reaction time. Theoretical M_w = conversion × ([monomer]/[initiator]); theoretical maximum M_w = 76 000 (PPBDb) and 52 000 (PPBDd).

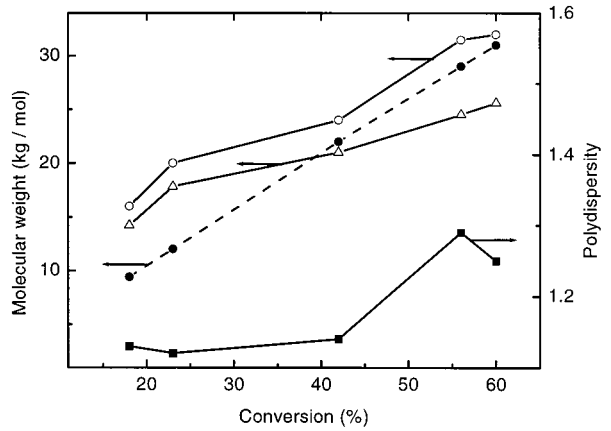


Figure 2. Kinetic study on PPBDd: molecular weight (M_n, open triangles; M_w, open circles), theoretical molecular weight (M_w, filled circles), and polydispersity (filled squares) as a function of monomer conversion.

spectra between 124 and 128 ppm. The P(PBD-*b*-3PV) block copolymer was not soluble enough to get a well-defined ^{13}C NMR spectrum. However, the spectrum of the diblock presents the same resonances as that of PPBDa, but with a poor resolution, and additional resonance peaks appear around 126 ppm which are attributed to the sp^2 carbon atoms of the three phenyl rings and the two double bonds of the 3PV part.

SEC. The molecular weights were obtained by size exclusion chromatography (SEC) in eluent THF with the coupled detection of refractive index and light scattering (Spectra Physics 1000 system equipped with a Shodex RI-71 refractive index detector, white light, coupled to a Dawn light scattering apparatus). The refractive increments were measured on a LDC Analytical KMX-16 laser differential refractometer at 630 nm. The d*n*/d*c* of PPBDa was measured in THF at 25 °C. A value of 0.253 mL/g was found. Data on vPBD polymerization are given in Table 1. We can see the molecular weight increase for PPBDb and PPBDd, especially during the first hours of polymerization. After 16 h, the molecular weight did not change significantly (ca. 1−3%). Kinetic results on PPBDd show an increase in molecular weight following the conversion, however not completely linearly (Figure 2). The self-initiated polymerization of vPBD in refluxing xylene led to high molecular weight, highly polydisperse PPBDe (Figure 3).

Data for the diblock P(PBD-*b*-3PV) and related homopolymers PPBDa and P3PV are summarized in Table 2; the chromatograms are given in Figure 4. A molecular weight M_w of 3.8×10^4 was detected for PPBDa, with a low polydispersity of about 1.21. The molecular weight M_w of the diblock P(PBD-*b*-3PV) was found to be 5.6×10^4, with a polydispersity of 1.53. On the basis of the raw SEC data and neglecting the presence

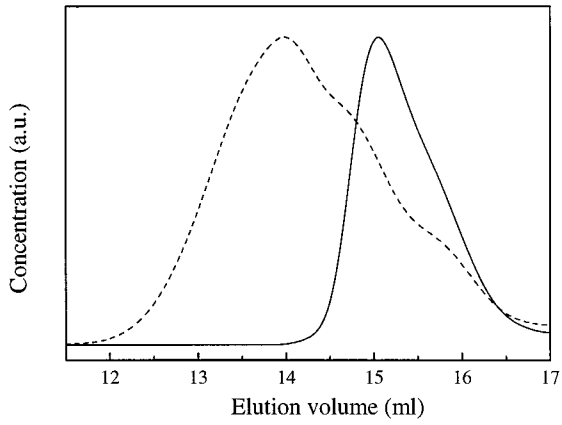


Figure 3. Comparison of TEMPO-controlled (PPBDc: continuous line) and self-initiated (PPBDe: dashed line) polymerization of vPBD. Size exclusion chromatograms of polymers eluted in THF.

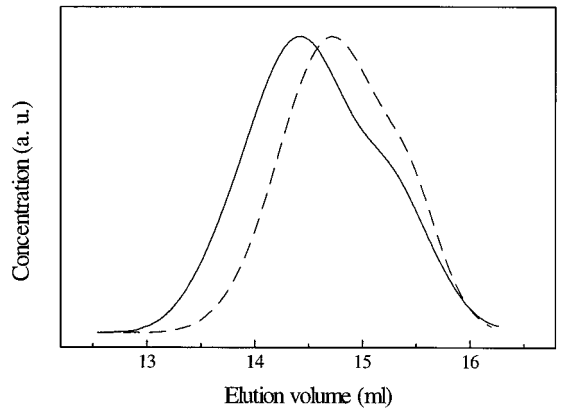


Figure 4. Size exclusion chromatograms of PPBDa (dashed line) and of diblock copolymer P(PBDa-*b*-3PV) (continuous line) eluted in THF.

Table 2. Polymer Characterization and Spectroscopic Data in THF Solutions of the P3PV, PPBDa, and P(PBD-*b*-3PV) Polymers

	P3PV	PPBDa	P(PBD-*b*-3PV)
isolated yield (%)	76	59	51
M_w (g/mol)	37000	38000	56000
polydispersity	1.5	1.21	1.53
λ_{max} absorption (nm)	361	311	309
ϵ (M^{-1} cm^{-1})	11200	50500	34400
λ_{max} emission (nm)	420	387	401
fluorescence yield (%)	85	50	60

of homopolymer, one calculates a PBD to 3PV monomer unit ratio of 2:1 for the block copolymer.

Thermal Properties. Thermogravimetric analyses of PPBDa and P(PBD-*b*-3PV) show a good thermal stability, with less than 1% weight loss at 300 °C and less than 10% weight loss at 400 °C.

Optical Properties. The ultraviolet absorption spectra were measured in THF solution with a SLM Aminco 3000 Array spectrophotometer. Fluorescence measurements were performed on a SLM Aminco SPF-500 spectrofluorometer. The fluorescence quantum yields in THF solution were determined relative to quinine sulfate in sulfuric acid (ϕ = 0.55).

Discussion

Previous studies on the v3PV monomer[16] showed that the TEMPO-mediated free-radical polymerization could be applied successfully to large functional monomers. The results obtained were much better than in the case of classical free-radical polymerization. But the low

reactivity of the monomer, due to the large delocalization of the radicals, induced longer reaction times (several days) and slightly higher polydispersity (1.5) than what is observed for simple monomers such as styrene.

Polymerization of vPBD under the same conditions appears to be very efficient. Homopolymer PPBDa exhibited a low polydispersity (1.21) and reasonably high molecular weight (38 000 g/mol). PPBDb, prepared under slightly different conditions (smaller quantities, increased dilution), showed a slightly broader distribution (ca. 1.3) and a higher molecular weight (63 000 g/mol). Using the unimolecular initiator **I** led to similar results in terms of conversion and polydispersity, while lower molecular weights were obtained by increasing the [initiator]/[monomer] ratio. The final conversions (50−60%) are higher than those observed in the case of vPBD classical (AIBN-initiated) free-radical polymerization.[26] These results are comparable with the values observed for polystyrene obtained via a similar route.[27,28] The kinetic studies carried out on PPBDb,d (Table 1, Figure 2) show a correlated increase of conversion and molecular weight vs reaction time, thus pleading for a quasi-living character of the polymerization. Low polydispersities (down to 1.15) can be obtained by limiting the reaction time (and therefore conversion); a major drawback of this strategy being the difficult removal of unreacted monomer by many successive reprecipitations. The deviation of the molecular weight measured for PPBDd from the theoretical molecular weight (assuming 100% initiation efficiency) is indicative of a slow initiation mechanism, which can also be an explanation for the increased polydispersity.

The reactivity of vPBD monomer is much better than that of v3PV: the polymerization appears to be almost complete after 15−16 h. This higher reactivity can be explained by the fact that the vPBD monomer is based on a biphenyl unit in which the delocalization should be less than in a distyrylbenzene unit. Whereas the enhanced reactivity allows shorter reaction times and narrower polydispersities in the TEMPO-mediated polymerization, the drawback of this reactivity is that vPBD self-polymerizes in refluxing xylene, then leading to a high molecular weight, highly polydisperse material (PPBDe, Figure 3). However, under the conditions we used (whether BPO/TEMPO or **I** is used as initiator), the TEMPO-mediated polymerization seems to efficiently compete with such a self-initiated polymerization, as seen on the molecular weight distribution (Table 1).

By reacting the isolated PPBDa polymer with v3PV monomer, we obtained a diblock copolymer P(PBD-*b*-3PV) (Scheme 2). Figure 4 presents the SEC diagrams of PPBDa and P(PBD-*b*-3PV). It clearly shows the increase of the molecular weight after adding the second monomer v3PV and results in an extension of the polymer chains by approximately half the length of the PBD block. The polydispersity of the diblock copolymer P(PBD-*b*-3PV) (1.53) is somewhat higher than that of the PPBD and does not compare so favorably with the values obtained on other "TEMPO diblocks", but it is consistent with the low reactivity of the second monomer. A partial inactivation of the PPBD chains (dead ends) cannot be neglected, which might be the reason for the increased polydispersity of the diblock copolymer. It can also explain the shape of the SEC diagrams of PPBDa and of P(PBD-*b*-3PV) at high elution volume,

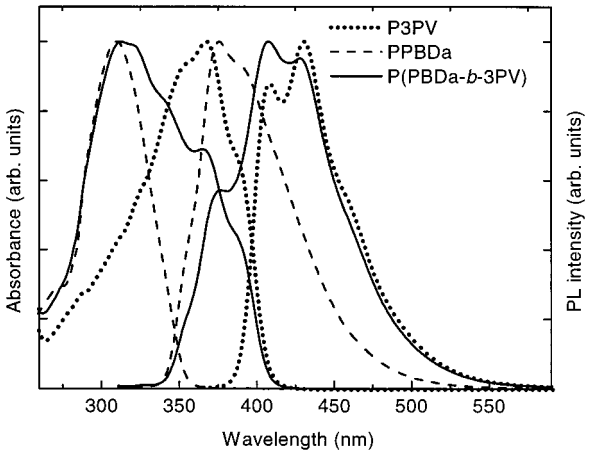


Figure 5. UV−vis absorption and photoluminescence spectra of PPBDa (- - -), P3PV (• • •), and P(PBDa-*b*-3PV) (—) in THF.

showing the presence of chains of the same relatively low molecular weight. The percentage of dead polymer chains is very difficult to quantify. However, it is noteworthy that this kind of copolymer can probably not be obtained by other polymerization techniques: these conjugated monomers are not suitable for anionic processes, due to the presence of reactive double bonds (v3PV) or acidic aromatic hydrogens (vPBD) that would give side reactions. Using classical free radical polymerization, no block copolymers can be obtained, and random copolymers would be unlikely to form due to the quite different reactivities of the monomers.

Figure 5 shows the UV−vis absorption spectra of the PPBDa, P3PV, and P(PBD-*b*-3PV) polymers in THF solution. The polymers present an absorption band in the near-UV, which is due to the conjugated phenylenevinylene and/or PBD parts. The maximum of absorption of the PBD part is at about 309 nm in both the homopolymer and the diblock copolymer. The λ_{max} of the 3PV part (367 nm) is at higher wavelengths, corresponding to a larger conjugation. This shift is consistent with a better electron delocalization for the phenylenevinylene system of the 3PV part compared to the biphenyl group of the PBD part.

Figure 5 gives also the fluorescence spectra (excitation wavelength at the absorption maximum) in THF solution of the polymers PPBDa, P3PV, and the diblock copolymer P(PBD-*b*-3PV). The emission peak of the PBD part is mainly in the near-UV, whereas the 3PV-part emission band is in the blue range of the visible spectrum. The fluorescence quantum yields of the polymers were measured at different excitation wavelengths. The values obtained for P3PV were around 85% (see Table 2). PPBDa presents a lower yield of 50%. A value of 60% was measured on the diblock P(PBD-*b*-3PV). The optical properties of the diblock copolymer in solution are a sum of the optical properties of the two homopolymers. The absorption spectrum (Figure 5) can be deduced by adding the spectra of the two separate polymers, normalized to the percentage of each block in the copolymer, and the emission spectrum (Figure 5) is very similar to that obtained from a mixture of the two homopolymers. Therefore, the block copolymer P(PBD-*b*-3PV) shows both a very strong absorption in the UV and an efficient fluorescence in the blue part of the visible spectrum.

Conclusion

In this work we have confirmed that the TEMPO-mediated free radical polymerization route offers a great potential for the preparation of side-chain functional polymers and diblock copolymers, the latter being impossible to obtain via classical polymerization techniques.

The vPBD monomer showed a very high reactivity with this polymerization technique and gave results comparable to what is observed for classical monomers like styrene. In particular, the isolated TEMPO-end-capped polymer showed a narrow polydispersity and was still able to initiate the polymerization of another monomer, making it possible to prepare diblock copolymers containing two different functional side chains.

The combination of two (or more) functionalities into a single polymer is a very promising approach to making advanced materials for polymer-based electronic devices, since it can greatly simplify the processing steps. Tailor-made block copolymers offer the advantage of ultimately controlling the morphology of the materials by varying the size of the different blocks. The diblock copolymer we described here is a typical example of such a material. It consists of a block with conjugated chromophores as side groups and a block bearing electron-transport units. These two functionalities are essential for adjusting the properties of semiconducting devices. Variation of the size of the different blocks and evaluation of the corresponding morphologies are now of prime importance for optimizing the applicability of this new material.

Acknowledgment. The Dutch Organization of Technology (SON/STW), the Commission of the European Communities (Human Capital and Mobility program), and the Netherlands Organization for Scientific Research, Physics Division (NWO-FOM), financially supported this work. P. F. van Hutten and S. C. Veenstra are gratefully acknowledged for their assistance.

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MA0115850